Regioselective iodine addition to the metal-metal bond of a carboxamido triosmium cluster

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Phenylacetaldehyde. Phenylacetylene (10 mmol, 1.02 g) was hydroborated with disiamylborane (20 mmol, 20 mL) for 1 h. The resultant vinylorganoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) at room temperature for 2 h. GLC analysis (SE-30) indicated a 97% yield of phenylacetaldehyde. Distillation afforded 1.03 g (86%) of phenylacetaldehyde: bp 76–78 °C (8 mmHg) [lit.[25] bp 88 °C (18 mmHg)]; ^1H NMR ($CDCl_3$), δ 2.8 (d, J = 7 Hz, 2 H, CH_2), 7.1 (s, 5 H, ArH), 9.8 (s, 1 H, CHO).

4-Octanone. 3-Octyne (10 mmol, 1.1 g) was hydroborated with disiamylborane (20 mmol, 20 mL) for 1 h. The resultant vinylorganoborane was oxidized by adding water (10 mL) and sodium percarbonate (3.69 g, equivalent to 30 mmol of hydrogen peroxide) at room temperature for 2 h. GLC analysis (SE-30) indicated a 100% yield of 4-octanone. Distillation afforded 1.0 g (85%) of 4-octanone: bp 75–77 °C (40 mmHg) [lit.[25] bp 70 °C (26 mmHg)]; ^1H NMR ($CDCl_3$) δ 1.0 (t, J = 7 Hz, 6 H, CH_3), 1.5 (m, 6 H, CH_2), 2.5 (t, J = 7 Hz, 4 H, 2 CH_2CO).

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Regioselective Iodine Addition to the Metal–Metal Bond of a Carboxamido Triosmium Cluster

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Summary: The triosmium complex $HOs_3(CO)_{10}$-$(OCNHCHMe_2)I_2$ (**3b**) was isolated as a minor product from the reaction of $HOs_3(CO)_{10}(OCNHCHMe_2)$ (**1**) with I_2. An X-ray characterization of **3b** reveals that the unsymmetrical carboxamido ligand controls the regioselective addition of the iodine molecule onto the M–M bond. The species that result from the cleavage of different M–M bonds exhibit distinctive chemical reactivities. The cleavage of the Os–Os bond neighboring the Os atom with oxygen coordination yields the stable complex **3b**. However, the cleavage of the other nonbridged Os–Os bond gives the isomeric intermediate **3a**, which then reacts with another I_2 to form the dinuclear complex $Os_2(CO)_6(OCNHR)I_3$ (**2-*cis***). The difference between the reactivities of **3b** and **3a** demonstrates the influence of the activating ability of the oxygen atom of the carboxamido ligand.

The addition of an I_2 molecule to $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OCNHCHMe_2)$ (1) causes a cleavage of the trinuclear cluster.[1] The reaction produces two kinetic products, the mononuclear *trans*-$HOs(CO)_4I$ (4-*trans*) and the dinuclear osmium complex *cis*-$(\mu\text{-}I)Os_2(CO)_6(\mu\text{-}OCNHCHMe_2)I_2$ (2-*cis*).[2a] Complex 4-*trans* then transforms to the thermodynamically more stable complex 4-*cis*.[1] Recently we found that 2-*cis* in solution slowly isomerizes to the more stable 2-*trans*.[2b] The production of two kinetic compounds indicates that the reaction should be controlled by an as yet unspecified pathway. Described herein are the results of the spectroscopic observation of an intermediate, which we propose as $(\mu\text{-}H)Os_3(CO)_{10}(\mu\text{-}OCNHCHMe_2)I_2$ (**3a**), and the isolation of the minor isomeric complex **3b**. An X-ray characterization of **3b** reveals a regioselective addition of the iodine molecule to the triosmium cluster, controlled by the presence of the unsymmetrical carboxamido ligand,[3] and implies a stereospecific control of two kinetic products.

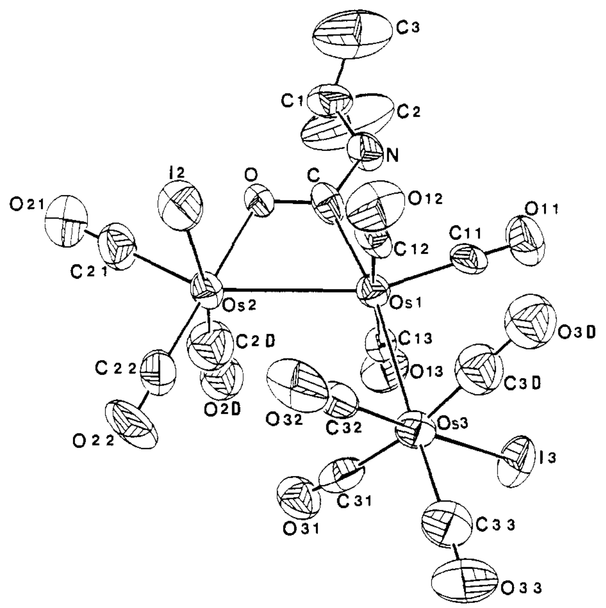

Figure 1. ORTEP disgram of $HOs_3(CO)_{10}(OCNHCHMe_2)i_2$ (**3b**), showing the atom-labeling scheme. Selected bond distances (Å) and bond angles (deg) are as follows: Os(1)–Os(2), 3.1115 (14); Os(1)–Os(3), 2.9545 (16); Os(1)–C, 2.096 (16); O–C, 1.281 (17); C–N, 1.362 (18); N–C(1), 1.484 (21); Os(2)–I(2), 2.7163 (18); Os(2)–O, 2.085 (9); Os(3)–I(3), 2.7343 (25); Os(2)–Os(1)–Os(3), 108.05 (4); Os(1)–Os(3)–I(3), 92.60 (6); Os(2)–Os(1)–C, 62.9 (4); Os(3)–Os(1)–C, 170.9 (4); C–Os(1)–C(11), 96.9 (6); C–Os(1)–C(12), 94.1 (6); C–Os(1)–C(13), 89.8 (6); Os(1)–Os(2)–I(2), 93.60 (5); Os(2)–O–C, 113.6 (9); Os(1)–Os(2)–O, 65.2 (3); Os(1)–C–O, 118.3 (10); Os(1)–C–N, 123.9 (11); O–C–N, 117.7 (14); C–N–C(1), 119.4 (13); I(2)–Os(2)–O, 89.0 (3); N–C(1)–C(2), 106.0 (15); N–C(1)–C(3), 105.2 (14); C(2)–C(1)–C(3), 113.7 (20).

A ^1H NMR examination of the freshly prepared CD_3COCD_3 solution containing complex 1 and 1 equiv of I_2 reveals the presence of four hydride species: 4-*trans*, complex 1, complex **3b**, and intermediate **3a**, at δ −11.8, −13.4, −16.9, and −18.2, respectively. The intensity of the resonance at δ −18.2 increases at first and then, with the simultaneous production of complexes 4-*trans* and 2-*cis*, slowly decreases, disappearing within 2 h. This indicates that the species with the hydride peak at δ −18.2 is the intermediate that leads to complexes 2-*cis* and 4-*trans*. The intermediate is too active to be isolated, and its structure cannot be discerned from the NMR data alone.

The minor complex **3b**, with a resonance at δ −16.9, however, is stable and can be purified by column chromatography and isolated as a microcrystalline solid, with an optimum yield of 15% when carried out at 0 °C. This complex was spectroscopically characterized and has been fully defined by an X-ray diffraction study (Figure 1). Two of the three M–M separations are within 3.12 Å, indicating the existence of two metal–metal bonds. For a noncyclic triosmium system, in which one of the terminal

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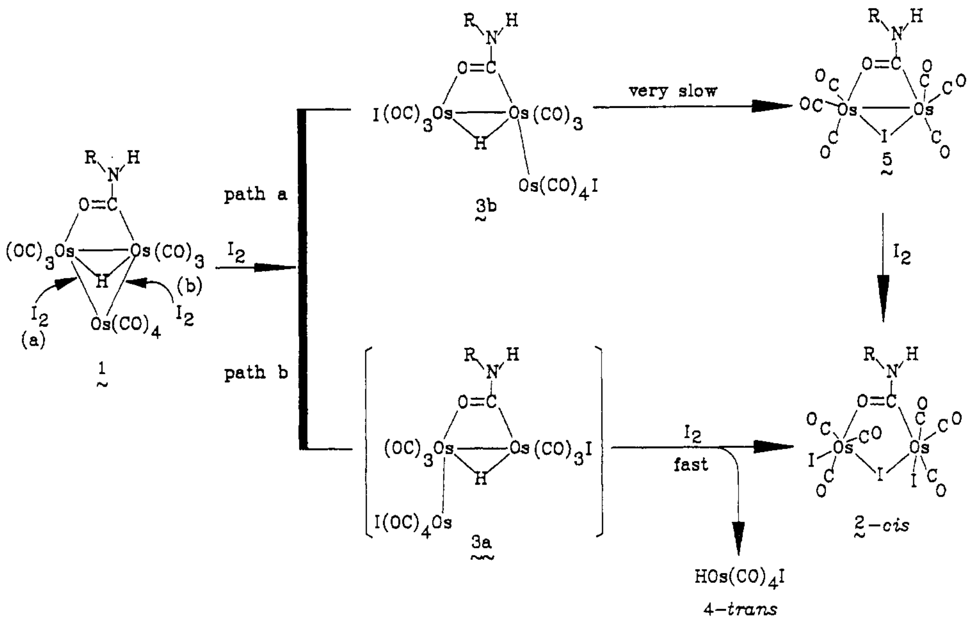
Scheme I



Os atoms is not bridged by any ligand, as is the case in **3b**, it is normal to have a linear structure ($\angle$Os–Os–Os > 169°).[4] The structure of **3b**, however, is bent. This particular type of triosmium system, which, to our knowledge, has not been previously reported, could result from a restricted exchange process[5] between Os(CO)$_4$I and CO, imposed by the presence of the carboxamido ligand. The two iodine atoms in **3b**, just as in the linear triosmium system Os$_3$(CO)$_{12}$I$_2$,[6] occupy positions far away from each other in order to minimize steric requirements.

It is clear that complex **3b** originates from the oxidative cleavage of one nonbridged Os–Os bond of complex 1 by one iodine molecule. From the structure of **3b** and stoichiometric considerations, we infer that complex 1 reacts with 1 equiv of I$_2$ to form intermediate **3a**, followed by a reaction with another 1 equiv of I$_2$ to yield the two kinetic products 2-*cis* and 4-*trans*. The addition of the first I$_2$ molecule should be limited to the two M–M bonds not bridged by the carboxamido and hydride ligands. Not only would the presence of these bridging ligands hinder the approach of the I$_2$ molecule but also the addition of I$_2$ across the bridged M–M bond would result in two seven-coordinated osmium metal centers and a hydride bridging the two nonbonded Os atoms, a case that rarely occurs in osmium complexes.[7] Furthermore, the entering of iodine usually breaks a M–M bond and displaces a hydride simultaneously.[8] That the bridging hydride could change to a terminal bonding mode during the addition of I$_2$ is highly unlikely since the observed hydride peak at δ −18.2 is within the values for bridging hydrides.[9]

We assume, therefore, that the intermediate **3a** derives from an oxidative cleavage of the other nonbridged Os–Os bond of complex 1 (see Scheme I). Complexes **3a** and **3b**, obtained from the cleavage of different Os–Os bonds of the triosmium cluster, show distinctively different chemical reactivities: while **3b** is relatively stable, complex **3a** reacts rapidly with another I$_2$ molecule to form the two kinetic products.

The higher reactivity of 3a could be interpreted as the activation of the M–M bond that results from the cis-labilizing ability of the oxygen atom of the carboxamido ligand. Examples illustrative of the CO-labilizing ability of oxygen donor ligands are found in the literature involving metal carbonyls containing phosphine oxides and formate ligands.[10] Further evidence is provided by the structure of the phosphine substitution product of the carboxamido complex, which contains the phosphorus ligand attached to the metal atom in a position cis to the oxygen atom. In several complexes of this type, the longest M–CO separations are also found to be located cis to the oxygen atom.[1,2] The cis labilization of halide could also be operative on activating the M–M bond with respect to I$_2$ addition.[10] By a comparison of the reactivities of **3b** and **3a**, however, it is clear that the activating ability solely derived from the terminal I ligand is not strong enough to cause the M–M bond cleavage.

In the second oxidative cleavage of the Os–Os bond, I$_2$ is added stereospecifically to give the final kinetic product 2-*cis*. In both I$_2$ additions,[11] the triosmium cluster most

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likely forms an adduct with I_2. Such a process would account for the formation of the kinetic products **2**-*cis* and **4**-*trans*. The formation of the kinetic complexes **4**-*trans* and **2**-*cis* from **3a** possibly occurs in two steps. For such a mechanism, a reductive elimination of $HOs(CO)_4I$ should take place in a stereospecific manner and should yield the kinetic product **4**-*trans* and, concomitantly, the dinuclear complex $Os_2(CO)_6(OCNHR)(\mu\text{-}I)$ (**5**). The concerted addition of I_2 across the metal–metal bond of the complex **5** should then produce the dinuclear complex **2**-*cis*. In support of the proposed mechanism, it is significant that, in the absence of I_2, **3b** slowly decomposes in about 20 days, producing complex **5** in a moderate yield, and that the reaction of **5** with I_2 quickly affords **2**-*cis* (see Scheme I). A single-step process from **3a** to **2**-*cis* cannot be ruled out, even though it is less likely.

In conclusion, the addition of I_2 to the triosmium cluster demonstrates the influence of the oxygen atom of the unsymmetrically bonded carboxamido ligand upon the cleavage of the Os–Os bond. Moreover, the stereospecificity of the products provides evidence for a concerted additions of I_2. I_2 addition to similar clusters with one or more unsymmetrical bridging ligands is currently under investigation.

Experimental Section

General Conditions. Standard inert-atmosphere techniques were used for the manipulation of all reagents and reaction products. Infrared spectra were recorded on a Perkin-Elmer Model 983 spectrometer. The ^{1}H and ^{13}C NMR spectra were taken on a Bruker AM-300WB spectrometer at ambient temperature. Electron impact mass spectra were recorded on a JEOL JMS D-300 spectrometer. Solvents were rigorously dried with appropriate drying agents and distilled before use. $HOs_3(CO)_{10}(OCNHR)$ was prepared by literature methods.[1]

Isolation of $HOs_3(CO)_{10}(OCNHCHMe_2)I_2$ (3b). To a solution of 373 mg (0.40 mmol) of $HOs_3(CO)_{10}(OCNHR)$ in 10 mL of acetone, in an ice bath, was added 143 mg of I_2. The solution was stirred at ambient temperature for 4 h, during which time a white precipitate was apparent. Filtration of the mixture afforded **2**-*cis*, as a white powder. The solvent of the filtrate was removed under vacuum, and the residue was extracted with hexane (4 × 15 mL). The volume of hexane was reduced to about 5 mL; then the mixture was passed through a silica gel packed column by using 30% dichloromethane–70% hexane as the eluent. The yellow product (second band, 70 mg; 15%) was recrystallized from hexane. ^{1}H NMR ($CDCl_3$): δ 5.88 (d, broad doublet, 1 H, NH), 4.22 (m, 1 H, CH), 1.18 (dd, 6 H, 2 Me), –16.9 (s, 1 H, hydride). ^{13}C NMR ($CDCl_3$): δ 170.51 (carboxamido C), 184.18, 182.76, 176.31, 175.43, 175.38, 169.94, 166.65, 165.13, 163.30, 160.82 (10 terminal CO's), 44.75 (CH), 23.06, 22.48 (2 Me). IR (ν_{CO}, in C_2Cl_4, cm^{-1}): 2125 (w), 2115 (m), 2082 (m), 2043 (s), 2025 (m), 2018 (w, sh), 2005 (m), 1999 (w), 1986 (w). Mass spectrum: parent peak observed at *m/e* 1195; peaks attributed to each of the 10 CO losses also observed at *m/e* 1166, 1138, 1110, 1082, 1054, 1026, 998, 970, 942, and 914, respectively. Anal. Calcd for **3b**: C, 14.06; H, 0.75. Found: C, 14.39; H, 0.68.

Structure Determination of 3b. Crystals of **3b** were grown from hexane as yellow cubes. The dimensions of the crystal chosen for X-ray diffraction were 0.50 × 0.48 × 0.38 mm. This crystal was mounted on a CAD4 four-circle diffractometer, and intensities were collected for $4 < 2\theta < 50°$ according to the methods described earlier.[1] The data were processed with the following lattice parameters: $a = 9.030$ (6) Å, $b = 24.522$ (4) Å, $c = 11.783$ (4) Å, $\beta = 105.59$ (4)°. The space group, based on the systematic absences, was uniquely assigned as $P2_1/n$. The volume was 2513 (2) Å^3, and the calculated density was 3.174 g/cm^3. Of the total 4708 reflections, 3089 independent intensities having $I > 2.5\sigma(I)$ were deemed "observed", and only these were used in the solution and refinement of the structure. Data were corrected for Lorentz–polarization effects, and an empirical absorption correction was applied on the basis of azimuthal rotation. The iodine and osmium atoms were located by Patterson methods, and the carbon, oxygen, and nitrogen atoms were located by successive electron-density difference syntheses. Two CO ligands, CO(2D) and CO(3D), and two iodine ligands were disordered and were refined with partial occupancies. The structure was refined by full-matrix least squares with anisotropic thermal parameters for all the non-hydrogen atoms except those disordered CO's. The refinement converged to $R = 0.043$ and $R_w = 0.032$. All intramolecular bond distances and angles are within normal ranges except those in disorder.

Isolation of $Os_2(CO)_6(OCNHCHMe_2)(\mu\text{-}I)$ (5). Complex **3b** (30 mg, 0.025 mmol), isolated as described above, was stored under nitrogen in $CHCl_3$ for ca. 20 days, during which time transformation of complex **3b** to **5** took place. Complex **5** was also purified by column chromatography (second band) by using 30% dichloromethane–70% hexane as eluent (7 mg, 36%). ^{1}H NMR ($CDCl_3$): δ 5.52 (d, broad doublet, 1 H, NH), 3.97 (m, 1 H, CH), 1.05 (dd, 6 H, 2 Me). ^{13}C NMR ($CDCl_3$): δ 185.52 (carboxamido C), 179.02, 176.66, 176.59, 176.22, 175.90, 174.05 (6 terminal CO's) 43.10 (CH), 22.67, 22.36 (2 Me). Mass spectra show a parent ion envelope (*m/e* 765) accompanied by six envelopes corresponding to successive losses of CO from the parent ion.

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Supplementary Material Available: Listings of crystal and intensity collection data, fractional coordinates, isotropic thermal parameters, and complete bond distances and bond angles for **3b** (5 pages); a listing of observed and calculated structure factors for **3b** (15 pages). Ordering information is given on any current masthead page.

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^{207}Pb NMR Study on Transition-Metal-Substituted Organolead Complexes

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Summary: Chemical shift and coupling constant data for a variety of trimethyl-, triethyl-, and triphenyllead complexes of the transition-metal systems $Mn(CO)_5$, $(\eta^5\text{-}C_5H_5)M(CO)_n$ (M = Fe, Cr, Mo, W), and $Co(CO)_4$, and some of their phosphine-substituted derivatives, are reported. The variations in chemical shift closely resemble ^{119}Sn data obtained from a similar, but limited, set of Sn complexes but are somewhat more sensitive to chemical substitution on the lead atom. Changes in solvent and concentration do not produce major changes in chemical shift, suggesting that neither coordination by polar solvents nor self-association in solution are important in this series of complexes.

The synthesis of stable lead–metal complexes was published as early as 1941 by Hein and co-workers[1] and later by several other groups.[2-4] In general the complexes reported were stable crystalline materials of limited chem-

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